# A procedural development for the analysis of Fe-56/54 and Fe-57/54 isotope ratios with new generation IsoProbe MC-ICP-MS

# A procedural development for the analysis of $^{56/54}$Fe and $^{57/54}$Fe isotope ratios with new generation IsoProbe MC-ICP-MS.

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We have developed a procedure for iron isotope analysis using a hexapole collision cell MC-ICP-MS which is capable of Fe isotope ratio analysis using two different extraction modes. Matrix effects were minimised and the signal-to-background ratio was maximised using high-concentration samples (~ 5µg Fe) and introducing 1.8 mL/min Ar and 2 mL/min $H_2$ into the collision cell to decrease polyatomic interferences. The use of large intensity on the faraday cups considerably decreases the internal error of the ratios and ultimately, improves the external precision of a run. Standard bracketing correction for mass bias was possible when using hard extraction. Mass bias in soft extraction mode seems to show temporal instability that makes the standard bracketing inappropriate. The hexapole rf amplitude was decreased to 50 % to further decrease polyatomic interferences and promote the transmission of iron range masses. We routinely measure Fe isotopes with a precision of ± 0.05 ‰ and ± 0.12 ‰ (2σ) for $\delta^{56}$Fe and $\delta^{57}$Fe respectively.

Keywords: Fe isotopes, IsoProbe, MC-ICP-MS, hard extraction, soft extraction.

## Introduction

The field of transition metal geochemistry has seen increasing development throughout the last twenty years and particularly since the introduction of multi-collector inductively coupled mass spectrometry MC-ICP-MS.[1-3] Iron is the ninth most abundant element in the universe[4] with four stable isotopes: $^{54}$Fe (5.845 %), $^{56}$Fe (91.754 %), $^{57}$Fe (2.1191 %) and $^{58}$Fe (0.2819 %).[5] The first attempts to measure Fe isotopic ratios began 60 years ago.[6] Thermal ionisation mass spectrometry, TIMS, has been applied to iron since the 1980s (*e.g.* Walczyk[7]; Gotz & Heumann[8]; Bullen & McMahon[9]) with a precision down to ± 0.6 ‰ (2σ).[10,11] However, TIMS was challenging because of the large spectrometer mass discrimination (mass fractionation) and the low ionisation efficiency for Fe analysis (the first ionisation potential is 7.870 eV). MC-ICP-MS, characterised by a higher ionisation efficiency and a very stable mass bias (although larger than TIMS, from 3 to 6%/amu), has become the technique of choice since its development in the 1990s.

Fe isotope analysis has seen growing attention in the Earth and environmental sciences for its potential use for tracing biogeochemical cycles. Because of their relative small mass difference, it was generally agreed that Fe isotopes could fractionate in nature solely via biological assimilation and preferential uptake by organisms. Recent studies have now indicated that Fe isotope fractionation can also occur abiotically in low temperature aqueous systems[12-14] and at high temperature.[15-18]

The principal difficulty in measuring precisely and accurately Fe isotope ratios is the removal of polyatomic and atomic mass interferences induced by the Ar plasma. Additional interferences can be due to sample matrix. Among these interferences are $^{40}Ar^{14}N^+$ and $^{54}Cr^+$ on $^{54}Fe^+$, $^{40}Ar^{16}O^+$ on $^{56}Fe^+$, $^{40}Ar^{16}OH^+$ on $^{57}Fe^+$, and $^{40}Ar^{18}O^+$ and $^{58}Ni^+$ on $^{58}Fe^+$. Various strategies have been developed to reduce interferences created by the Ar plasma: i) sample desolvation and the use of high-concentration samples,[19-24] ii) cold plasma,[25,26] iii) collision cells[27-30] and iv) high resolution multi-collection.[31-33]

In this contribution, we detail a procedure developed for the analysis of Fe isotope ratios on a new generation GV Instruments (formerly Micromass) IsoProbe-P MC-ICP-MS at the Scottish Universities Environmental Research Centre (East Kilbride, UK). This instrument enables us to conduct the ion extraction in two modes: the hard and the soft extraction modes. Although Fe isotope ratios have been published using both extraction modes,[29,33] no study compares the effect of each mode on the external precision and the overall stability of the measurement of Fe isotope ratios. Therefore, we have inspected the effects of extraction voltage, sample uptake rate, the hexapole potential difference and the collision gases on the overall stability of Fe isotope analysis.

## Analytical materials and methods

### Samples and standards preparation

All samples used in this study are part of an experimental investigation of iron sulphide geochemistry; therefore all samples are synthetic iron sulphide species (FeS and $FeS_2$) and $Fe(II)_{aq}$. Solutions were prepared using 18.2 MΩcm deionised water. Fe and S source reagents were analytical grade $Fe(NH_4)_2(SO_4)_2.6H_2O$ and $Na_2S.9H_2O$ (Sigma Aldrich™) respectively. $HNO_3$ and HCl were twice distilled, HF was once distilled. Once experimentally synthesised, solid samples were separated and dissolved in 6 M HCl or concentrated $HNO_3$ depending on the mineral, taken to dryness and re-dissolved in 5 % v/v $HNO_3$. The solution was then effectively Fe(III) in nitric acid (S being removed as $H_2S$ gas), and thus no column separation chemistry was performed on our samples.

IRMM-014 (IRMM™) was used as a bracketing reference standard for the δ calculation, i.e. before and after each sample. The isotopic concentrations of IRMM-14 are in percent, 5.845 ± 0.023 (2σ) for $^{54}Fe$, 91.754 ± 0.024 for $^{56}Fe$, 2.1192 ± 0.0065 for $^{57}Fe$, and 0.2818 ± 0.0027 for $^{58}Fe$.[5] These concentrations are close to the natural Fe isotope distribution. IRMM-014 Fe wire was dissolved on a hot plate in 5 % v/v $HNO_3$. Our external standard for determination of precision was prepared from a 1 g/L Fe solution (J.T Baker™).

### Mass Spectrometry

Analyses were performed the GV Instruments (formerly Micromass) IsoProbe MC-ICP-MS. Table 1 summarises the routine instrumental settings for Fe isotope analysis. Mass 54, 56, 57 and 58 were measured simultaneously on the multi-collection faraday cups in a static mode (Fig. 1). Cr interferences were monitored on mass 52 for further correction on mass 54. However, since our samples were experimentally synthesised, Cr contributions were never detected. Ni interferences on mass 58 should be monitored on mass 60, but on our instrument, it was physically not possible to align mass 60 on any cup, the range of masses being so large. In the case of this study, that is not a problem since only $^{56/54}Fe$ and $^{57/54}Fe$ were required. Faraday cups were calibrated and displayed linear response over a 1 ppm to 8 ppm range. Typical response was 0.6 to 2 V/ppm and our sample solutions were 3 to 10 ppm Fe in 5% v/v $HNO_3$ (samples and/or standards) to obtain ~ 0.35 V on mass 54, ~ 6 V on mass 56, ~ 0.14 V on mass 57 and 0.024 V on mass 58.

Solutions were introduced into an ApexQ (Elemental Scientific™) inlet system which comprises a PFA nebuliser and a cyclonic desolvating spray chamber. The ApexQ was operated with Ar sweep gas and without the addition of $N_2$ to avoid further formation of $^{40}Ar^{14}N^+$ on mass 54. The condenser cooling temperature was set at 2°C and the temperature

of the spray chamber at 100°C. Both 50 µL/min and 100 µL/min uptake rates were investigated.

The instrument high tension was set at -6000 V. Ion extraction from the source into the mass analyser can be run in two modes, called hard and soft extraction. We routinely run our samples using the hard extraction mode at -250V but both approaches were investigated and the results will be described later.

The IsoProbe incorporates a hexapole to the standard MC-ICP-MS instrumentation - between the cones and the optics region - in order to reduce the ions' energy spread from ~ 30eV to ~ 1eV, allowing a single focusing magnetic sector analyser. Ions are transmitted with a mass resolution ~ 500 Δm/m which is not sufficient to separate Fe peaks from polyatomic interferences. Fe peaks can be separated from molecular interference peaks with a resolving power of ~3000[34] and flat peaks can be preserved with resolving power of ~9000 (High resolution[31]). To reduce or remove polyatomic interferences, the hexapole can be used as a reaction cell. The introduction of collision gases (Ar and $H_2$) into the hexapole induces a series of ion-molecule reactions leading to the decrease of argides, oxides and hydrides in the ion beam. 1.8 mL/min Ar and 2 mL/min $H_2$ were introduced into the hexapole collision cell to completely remove $^{40}Ar^{14}N^+$ and $^{40}Ar^{16}OH^+$ on mass 54 and mass 57 respectively, and to decrease $^{40}Ar^{16}O^+$ on mass 56 to 0.006 V which represents 0.1 % of the Fe peak. After subtraction, interference contributions were smaller than the analytical precision. There was no peak on mass 55 suggesting that $FeH^+$ did not form even at high Fe concentrations.

On-peak-zero correction was measured on a 5% v/v $HNO_3$ solution prior to each Fe solution (samples or standards). Data collection consisted of 5 blocks of 20 5 x 1s integrations, followed by a 4 min rinse in 5% v/v $HNO_3$ + 2% v/v HF. Mass bias was corrected using IRMM-014 as a bracketing standard (Eq. 1 and 2). The external standard was measured five times before the run of samples. During the run, one external standard was measured after every four samples.

Data are reported in conventional fashion using per mil δ notation, $\delta^{56}Fe$ and $\delta^{57}Fe$, defined as (1) and (2):

$$\delta^{56}Fe = \left( \frac{(^{56}Fe/^{54}Fe)sample}{(^{56}Fe/^{54}Fe)std} - 1 \right) \times 10^3 \qquad (1)$$

$$\delta^{57}Fe = \left( \frac{(^{57}Fe/^{54}Fe)sample}{(^{57}Fe/^{54}Fe)std} - 1 \right) \times 10^3 \qquad (2)$$

where *std* is the reference material *IRMM-014* (IRMM™).

## Procedural development

### Theoretical and observed errors

The external precision on $\delta^{56}$Fe and $\delta^{57}$Fe is given by the 95% reproducibility (2σ standard deviation) of the δ external standard repeated at least twelve times. The external precision should approximate the internal error of each individual ratio (2se) which is the 95% confidence limits on the mean ratio. Ludwig[35] showed that the internal error is the result of a combination of shot noise (error on the measurement of ions) and Johnson noise (from the Faraday amplifier). The overall theoretical error on a measured Fe isotope ratio is given by Eq. 3:

$$\%2se = 2 \times \frac{\frac{^{56}Fe}{^{54}Fe}\sqrt{\underbrace{\left(\frac{1}{V_{^{56}Fe}}+\frac{1}{V_{^{54}Fe}}\right)\times\left(\frac{1.6\times10^{-8}}{t}\right)}_{Shot-noise}+\underbrace{2\times0.000014^2\times\left(\frac{1}{V^2_{^{56}Fe}}+\frac{1}{V^2_{^{54}Fe}}\right)}_{Faraday-noise}}}{\sqrt{N}} \quad (3)$$

where V is the voltage on the peak and t is the time of the measurement (10 min).

It is intuitive to think that the larger the internal errors of the mean are, the larger the external error on the overall run should be. However, it is not possible to demonstrate this mathematically because in the 2sd calculation we do not take in account the internal error of each individual δ value. In Fig. 2A, we plot the mean 2se of the ratios during several run times against the external precision of the run. We demonstrated graphically that for the external precision to be ≤ ± 0.1 ‰ and ≤ ± 0.15 ‰ (2σ) for $\delta^{56}$Fe and $\delta^{57}$Fe, the internal error over a run time should not exceed ~0.0018% and ~0.0025% for $^{56/54}$Fe and $^{57/54}$Fe respectively. Rearranging Eq. 4 demonstrates that the voltage on $^{56}$Fe must be > 4V to produce such small errors, justifying the use of high-concentration samples. Collecting ~ 6V on mass 56 enables us to decrease the internal error down to 0.0013% (Fig. 2B). We could measure accurately Fe isotope ratios with an internal error (%2se) systematically < 0.0020 % and < 0.0030 % for $^{56/54}$Fe and $^{57/54}$Fe respectively. The precision of our measurements was ± 0.05 ‰ and ± 0.12 ‰ (2σ) for $\delta^{56}$Fe and $\delta^{57}$Fe respectively.

### Matrix effects and sample uptake

The reduction of interferences and their effects is crucial for precise and accurate measurements. This was achieved by the use of collision gases (see below) and maximising the source-to-background ratio by introduction of high-concentration samples (up to 10 ppm). Sample matrix is a potential source of interferences, with direct effects on the overall

reproducibility. We compared bracketing our external standard (Fe solution from J.T.Baker™) with bracketing IRMM-014 itself. The Baker solution, which is essentially an iron sulphate solution led to a reproducibility of ± 0.05 ‰ and ± 0.12 ‰ (2σ) for $\delta^{56}$Fe and $\delta^{57}$Fe respectively. IRMM-014 solution, which is dissolved Fe in $HNO_3$, bracketed with itself, led to a precision as good as ± 0.05 ‰ and ± 0.05 ‰ (2σ) for $\delta^{56}$Fe and $\delta^{57}$Fe respectively.

The uptake rate is determined by the diameter of the auto-sampler capillary. Both 50 μL/min and 100 μL/min uptake rates were used. Twice as much material was consumed using the 100 μL/min rate, doubling the sensitivity. However, the stability of a measurement was systematically decreased as well, leading to internal errors > 0.0050% and > 0.0100% for $^{56/54}$Fe and $^{57/54}$Fe respectively. As a result, the measured Fe isotope ratios which are the mean of the 100 integrations were not reproducible within an acceptable precision. We suspect that this uptake rate was too high for the ApexQ inlet system to quantitatively desolve the sample, leading to inconsistent variations in the signal.

We examined the effect of the Fe concentration matching between the samples and the reference standard IRMM-014 on the measured isotopic ratios. True ratios are obtained when both the sample and the standard have the same concentration (Fig. 3). The effect is more dramatic for $[Fe]_{sample}<[Fe]_{Std}$, as suggested by other authors.[22,36] We suspect that in this region, Fe concentration is small relative to the interferences and therefore the peaks are committed to variations in interference production from the plasma. The deviation from linear response is thus due to plasma behaviour and not detector non-linearity over that range.

**Extraction mode: hard versus soft extraction**

Both hard and soft extraction modes have been used in laboratories for the analysis of Fe isotopes.[29,30,37,38] The hard extraction mode applies a strong negative voltage to the cones (generally ~ -600V), while the soft extraction mode applies a small positive voltage to the cones (0 to 20V). The soft extraction mode has been available only on new generations of the IsoProbe, and has seen increasing interest since it considerably reduces molecular interferences and memory effects.[29] We investigated the stability of the measurement during 100 integrations of the analysis in both hard and soft extraction (Fig. 4). In hard extraction, internal errors (2se) produced on the ratios during 100 integrations (~ 10 min) are systematically less than 0.0020% and 0.0040% for $^{56/54}$Fe and $^{57/54}$Fe, while in soft extraction, internal errors are 0.0060% and 0.0100% for $^{56/54}$Fe and $^{57/54}$Fe respectively. In all the applications we have utilised soft extraction, we observe increased mass bias but this is not necessarily detrimental if mass bias is internally corrected. However, for stable isotope measurements of iron we need to make an external mass bias correction by reference to bracketing standards. In soft extraction mode there is an increased time-dependent mass bias

instability, even over timescales of a few minutes, compared to the hard extraction mode. As a result, a simple standard bracketing correction was not sufficient and the overall precision on long term runs was always > ± 0.2 ‰ and > ± 0.6 ‰ (2σ) for $\delta^{56}Fe$ and $\delta^{57}Fe$ respectively. We suspect that small voltage fluctuations in soft extraction mode have a more dramatic effect on mass bias than in hard extraction considering their voltage range (0 to 20V versus 0 to -1500V for soft and hard extraction respectively). Thirlwall and Anczkiewicz[39] did a comparative study for Hf, Nd and Pb isotopes using MC-ICP-MS and TIMS. They showed that for Nd isotope ratios, hard extraction produced a larger mass bias than soft extraction. This suggests that plasma chemistry and extraction voltage are not entirely comprehended yet.

Although hard extraction is usually operated at a cone voltage of ~ -600V or higher to maximise sensitivity, reducing the extraction potential to ~ -250 V was a key for successful Fe isotope measurements. At this voltage, molecular interferences on mass 52 are entirely removed, and transmission of masses 54, 56 and 57 is optimised. The instrumental mass bias is very stable and thus the standard bracketing technique is suitable.

**Hexapole tuning**

Hexapole tuning, i.e the rf amplitude (referred by some authors as Digital to analogue convertor settings, or D.A.C settings) and the introduction of collision gases plays a dominant role in optimising the transmission of ions. The IsoProbe collision cell can be used with two hexapole rf generator devices (6MΩ or 9MΩ), the 9 MΩ one being designed for measuring low mass elements. Reducing the rf amplitude to ~ 50 % enhances the transmission of low masses. In the literature, reported rf amplitudes vary from 40 % to 60 %.[29,30] The removal or reduction of $^{40}Ar^{14}N^+$ and $^{40}Ar^{16}O^+$, $^{40}Ar^{16}OH^+$, $^{40}Ar^{18}O^+$ and $FeH^+$ interferences was achieved by the introduction of collision gases (Ar and $H_2$) into the hexapole collision cell.[27-29,34,40] Arnold *et al.*[40] studied the mechanisms of polyatomic interferences removal and the behaviour of $^{40}Ar^{16}O^+$, $^{40}Ar^{16}OH^+$ when varying Ar:$H_2$ ratios, flow rates, and the rf amplitude of the hexapole. In our routine, the rf amplitude was set at 50 % which decreases $^{40}Ar^{16}OH^+$, as Arnold *et al.*[40] reported. Introducing 1.8 mL/min Ar into the hexapole removed completely $ArN^+$ interference on mass 54. We thus investigated the effect of different $H_2$ flow rates on the polyatomic interferences in a blank solution (Fig. 5). Introduction of $H_2$ has larger effects on $ArOH^+$ (mass 57) than on $ArO^+$ (mass 56). $ArOH^+$ interferences were completely removed with a $H_2$ flow rate of 2 mL/min.

**Fe isotope analysis of synthesised iron-sulfide minerals**

The procedure described above was applied to the analysis of synthetic iron sulphide species and $Fe(II)_{aq}$. Samples were standard bracketed with IRMM-014 and the precision was given by the external standard J.T.Baker Fe solution ($\delta^{56}Fe$ = -0.23 ± 0.05 ‰ and $\delta^{57}Fe$ -0.35 ± 0.12

‰, Fig. 6). Marechal *et al.*[41] demonstrated that Zn mass bias on their VG Plasma 54 instrument was best fitted with an exponential law. In the case of Fe, the expected mass bias slopes obtained with the power and the exponential laws are given respectively by Eq. 4 & Eq. 5[42]:

$$slope_{56/54}^{57/54} = \frac{M_{57Fe} - M_{54Fe}}{M_{56Fe} - M_{54Fe}} = 1.501 \qquad (4)$$

$$slope_{56/54}^{57/54} = \frac{\ln(M_{57Fe} / M_{54Fe})}{\ln(M_{56Fe} / M_{54Fe})} = 1.488 \qquad (5)$$

where M is the atomic mass of the nuclide.

Our raw measurements all plot on the same mass fractionation line in a ln($^{57}$Fe/$^{54}$Fe) versus ln($^{56}$Fe/$^{54}$Fe) graph (Fig. 7), with a slope of 1.549 ± 0.003 which is consistent with Fe isotope mass difference. When standard-bracketing corrected, our data ($\delta^{56}$Fe and $\delta^{57}$Fe) plot on the terrestrial mass fractionation line with a slope of 1.52 ± 0.02 (Fig. 8). Our experimental work on synthesised FeS and $FeS_2$ from $Fe(II)_{aq}$ shows large Fe isotope fractionations. These results are preliminary and further experimental data are needed.

## Conclusion

We have developed a procedure for the analysis of $^{56}$Fe/$^{54}$Fe and $^{57}$Fe/$^{54}$Fe ratios on a hexapole collision cell MC-ICP-MS with a precision of ± 0.05 ‰ and ± 0.12 ‰ (2σ) for $\delta^{56}$Fe and $\delta^{57}$Fe respectively. This precision was achieved maximising the signal-to-background ratio by using high-concentration samples (3 to 10 ppm) and introducing Ar and $H_2$ gases into the hexapole collision cell. On our instrument, precise measurements are more readily achieved using hard extraction, although in this mode the $ArO^+$ interference at mass 56 was not entirely removed. However, in hard extraction mode the instrument showed relatively stable mass bias characteristics that allow the phenomenon to be corrected by sample-standard bracketing. In soft extraction mode we observed temporal instability in mass bias to the extent that sample-standard bracketing does not provide a reliable mass bias correction.

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## References


1. A. J. Walder and P. A. Freedman, *J. Anal. At. Spectrom*, 1992, **7**, 571.
2. A. J. Walder, A. I. Platzner and P. A. Freedman, *J. Anal. At. Spectrom*, 1993, **8**.
3. A. N. Halliday, D. C. Lee, J. N. Christensen, M. Rehkamper, W. Li, X. Luo, C. M. Hall, C. J. Ballentine, T. Pettlee and C. Stirling, *Geochim. Cosmochim. Acta*, 1998, **62**, 919-940.
4. E. Anders and N. Grevesse, *Geochim. Cosmochim. Acta*, 1989, **53**, 197-214.
5. P. D. P. Taylor, R. Maeck and P. De Bievre, *Int. J. Mass Spectrom. Ion Proc.*, 1992, **121**, 111-125.
6. G. E. Valley and H. H. Anderson, *J. Am. Chem. Soc.*, 1947, **69**, 1871-1875.
7. T. Walczyk, *int. J. Mass Spectrom. Ion Proc.*, 1997, **161**, 217-227.
8. A. Gotz and K. G. Heumann, *Int. J. Mass Spectrom. Ion Proc.*, 1988, **83**, 319-330.
9. T. D. Bullen and P. M. McMahon, *Mineral. Mag.* , 1998, **62A**, 255-256.
10. C. M. Johnson and B. L. Beard, *Int. J. Mass Spectrom. Ion Proc.*, 1999, **193**, 87-99.
11. B. L. Beard and C. M. Johnson, *Geochim. Cosmochim. Acta* 1999, **63**, 1653-1660.
12. C. M. Johnson, J. L. Skulan, B. L. Beard, H. Sun, K. H. Nealson and P. S. Braterman, *Earth and Planetary Science Letters*, 2002, **195**, 141-153.
13. I. B. Butler, C. Archer, D. Vance, A. Oldroyd and D. Rickard, *Earth and Planet. Science Letters*, 2005, **236**.
14. S. Severmann, C. M. Johnson, B. L. Beard and J. McManus, *Geochim Cosmochim Acta*, 2006, **70**, 2006–2022.
15. N. Dauphas, *Meteoritics Planet. Sci.*, 2007, **42**, 1597-1614.
16. A. Shahar, E. D. Young and C. E. Manning, *Earth and Planet. Science Letters*, 2008, **268**, 330–338.
17. F. M. Richter, N. Dauphas and F.-Z. Teng, *Chemical Geology*, 2009, **258**, 92-103.
18. M. Roskosz, B. Luais, H. C. Watson, M. J. Toplis, C. M. O. D. Alexander and B. O. Mysen, *Earth and Planetary Science Letters*, 2006, **248**, 851-867.
19. A. D. Anbar, J. E. Roe, J. Barling and K. H. Nealson, *Science*, 2000, **288**, 126-128.
20. J. E. Roe, A. D. Anbar and J. Barling, *Chem. Geol.*, 2003, **195**.
21. M. Sharma, M. Polizzotto and A. D. Anbar, *Earth. Planet. Sci. Lett.*, 2001, **194**.
22. N. S. Belshaw, X. K. Zhu, Y. Guo and R. K. O'Nions, *Int. J. Mass Spectrom*, 2000, **197**, 191-195.
23. G. L. Arnold, S. Weyer and A. D. Anbar, *Analytical Chemistry*, 2004, **76**, 322-327.
24. R. Schoenberg and F. von Blanckenburg, *International Journal of Mass Spectrometry*, 2005, **242**, 257-272.

25. K. Kehm, E. H. Hauri, C. M. Alexander and R. W. Carlson, *Geochim Cosmochim Acta*, 2003, **67**.
26. T. Walczyk and F. von Blanckenburg, *Science*, 2002, **295**, 2065 - 2066.
27. B. L. Beard, C. M. Johnson, J. L. Skulan, K. H. Nealson, L. Cox and H. Sun, *Chem. Geol.*, 2003, **195**, 87-117.
28. O. Rouxel, N. Dobbek, J. Ludden and Y. Fouquet, *Chem. Geol.*, 2003, **202**, 155-182.
29. N. Dauphas, P. E. Janney, R. A. Mendybaev, M. Wadhwa, F. M. Richter, A. M. Davis, M. van Zuilen, R. Hines and C. N. Foley, *Anal. Chem.*, 2004, **76**, 5855-5863.
30. E. Mullane, S. S. Russell, M. Gounelle, T. Mason, V. Din, D. Weiss and B. Coles, *In plasma source mass spectrometry: Applications and emerging technologies. London: The Royal Society of Chemistry.*, 2003, 351-361.
31. S. Weyer and J. Schwieters, *Int. J. Mass Spectrom. Ion Proc.*, 2003, **226**, 355-368.
32. F. Poitrasson and R. Freydier, *Chemical Geology*, 2005, **222**, 132-147.
33. N. Dauphas, A. Pourmand and F.-Z. Teng, *Chemical Geology*, 2009, **267**, 175-184.
34. J. Vogl, P. Klingbeil, W. Pritzkow and G. Riebe, *Journal of Analytical Atomic Spectrometry*, 2003, **18**, 1125 - 1132.
35. K. R. Ludwig, *U.S.G.S. Bull.*, 1986, **1622**, 219-221.
36. C. Archer and D. Vance, *J. Anal. At. Spectrom*, 2004, **19**, 656-665.
37. C. Archer and D. Vance, *Geology*, 2006, **34**, 153-156.
38. A. Thompson, J. Ruiz, O. A. Chadwick, M. Titus and J. Chorover, *Chemical Geology*, 2007, **238**, 72-83.
39. M. F. Thirlwall and R. Anczkiewicz, *International Journal of Mass Spectrometry*, 2004, **235**, 59-81.
40. T. Arnold, J. N. Harvey and D. J. Weiss, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 2008, **63**, 666-672.
41. C. N. Marechal, P. Telouk and F. Albarede, *Chem. Geol.*, 1999, **156**, 251-273.
42. F. Albarede and B. Beard, *Reviews in Mineralogy & Geochemistry*, 2004, **55**, 113-152.

***List of tables:***

**Table 1**: IsoProbe settings. Tuning parameters are followed by an asterisk.

***Figure captions:***

**Figure 1**: alignment of the cups for simultaneous measurements of masses 52, 54, 56, 57 and 58.

**Figure 2**: A: Empirical relationship between the mean of 2se during one set of measurement and the overall external precision of the run. B: Influence of the peak intensity (mass 56) on the theoretical error of the ratio $^{56/54}$Fe.

**Figure 3**: Concentration matching between samples and bracketing standards. Data plot on a mass fractionation line when both standards and samples have the same concentration.

**Figure 4**: Comparison of soft and hard extraction modes. A: variations of the measured ratio with time (100 integrations ~ 10 min). B: Mass bias associated with time (same data as A). C: Resulting fractionation lines on a long sample run.

**Figure 5**: A: Influence of the $H_2$ flow rate on polyatomic interferences. Ar flow rate is set at 1.8 mL/min. B: Resulting Fe isotope spectrum after the decrease of the interferences.

**Figure 6**: External precision given by the reproducibility of the measurement of a standard.

**Figure 7**: log-log plot of the row data. Error bars are included in the data point.

**Figure 8**: plot of $\delta^{57}$Fe versus $\delta^{56}$Fe for iron sulphide species. Error bars are given by the reproducibility 2 SD of the external standard.

Table 1

| | | | | | |
|---|---|---|---|---|---|
| **ApexQ** | | **Argon flow rates*:** | | **Torch position*** | |
| Cooling | 2 °C | Cooling | 13.50 L/min | Vertical | -0.6 |
| Heating chamber | 100°C | Intermediate | 1.35 L/min | Horizontal | -0.6 |
| Neb 2 | none | Nebuliser | 0.85 L/min | Axial | 4 |
| Uptake rate | ~ 50 µL/min | | | | |
| **Interface** | | **Hexapole gases** | | **Extraction** | |
| Skimmer Cone | Ni | Ar | 1.8 mL/min | rf power | 1350 W |
| Sample Cone | Ni | $H_2$ | 2 mL/min | Extraction voltage* | -250 V (Hard) |
| | | | | High Tension* | - 6000 V |
| **Analysis** | | | | Hexapole rf amplitude* | 50% |
| Sample concentration* | 3- 10 ppm | | | | |
| Mode | static | | | | |
| Cup position | | | | | |
| | *Elementar interferences* | *Molecular interferences* | *Isotopes of interest* | | |
| L2 | $^{52}$Cr | | | | |
| Ax | $^{54}$Cr | ArN | $^{54}$Fe | | |
| H1 | | ArO | $^{56}$Fe | | |
| H4 | | ArOH | $^{57}$Fe | | |
| H7 | $^{58}$Ni | ArO | $^{58}$Fe | | |

Figure 1

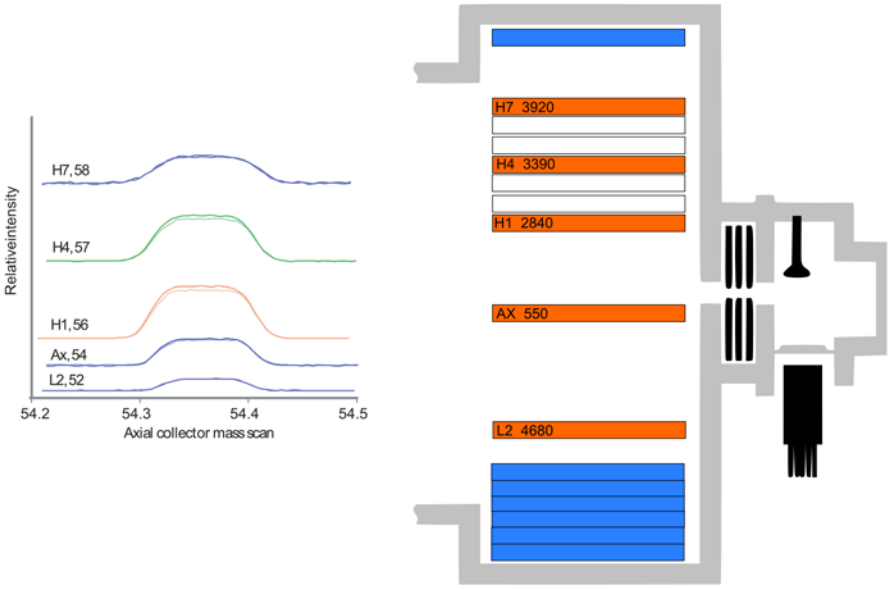


Figure 2

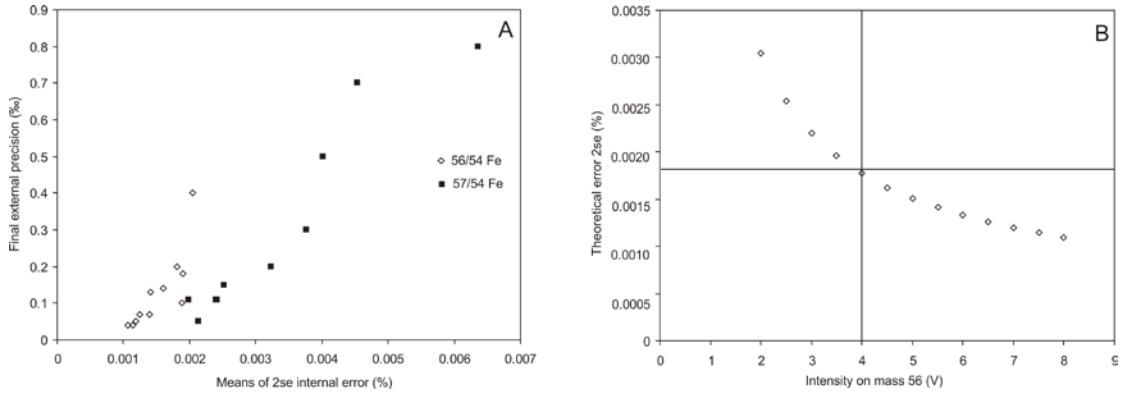


Figure 3

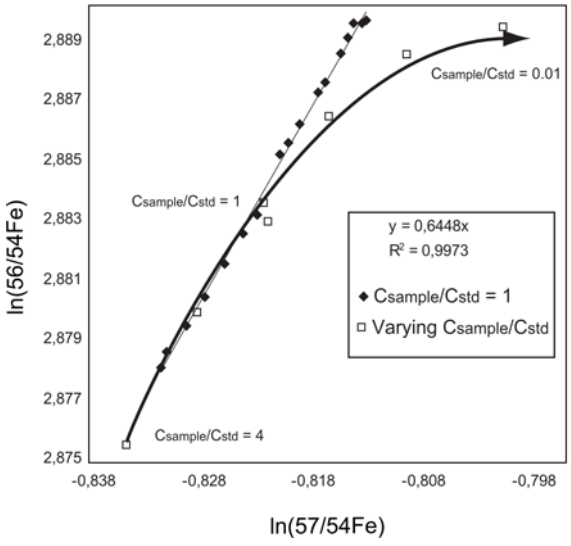

Figure 4

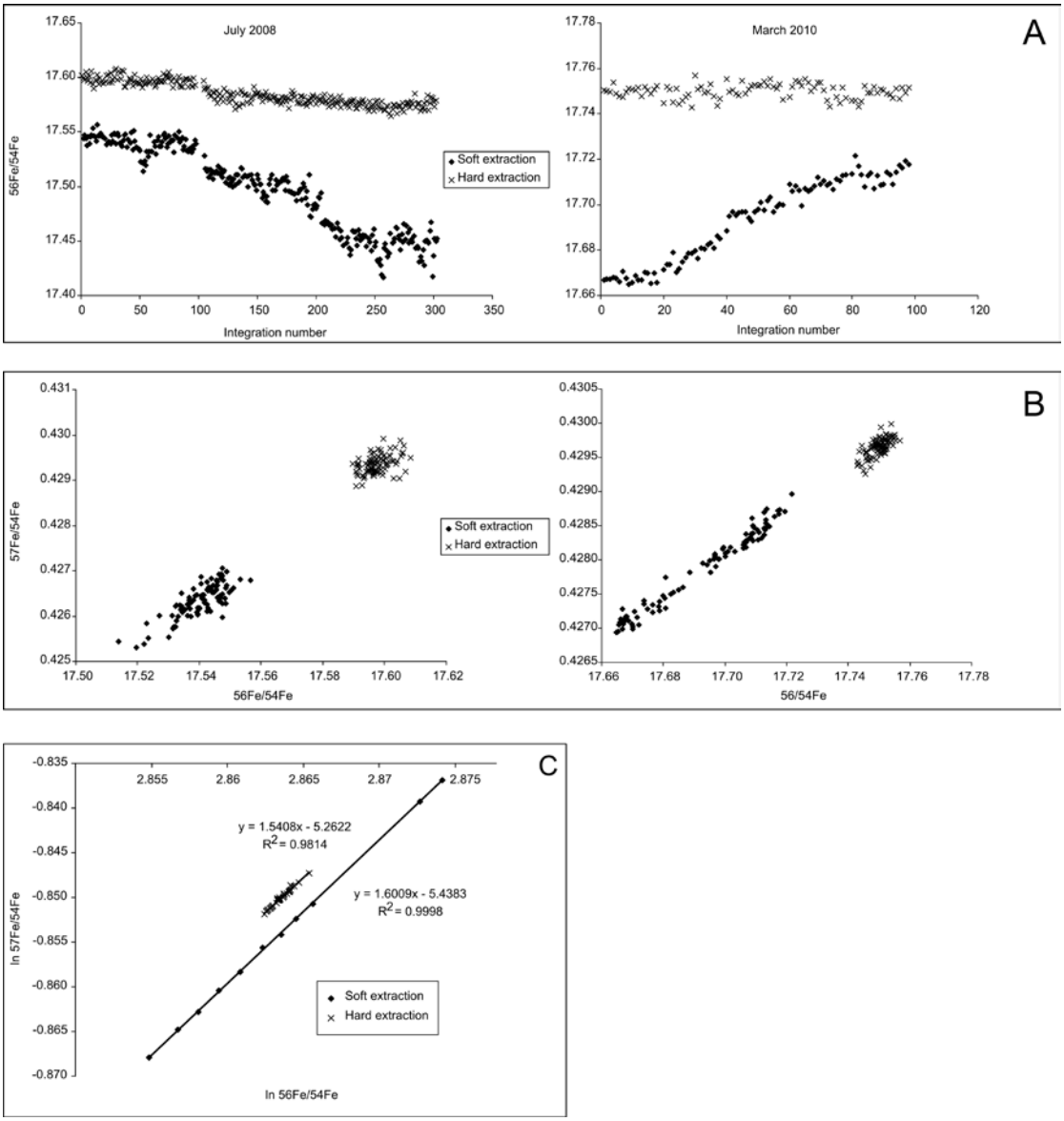
A
July 2008
March 2010
56Fe/54Fe
Integration number
Soft extraction
Hard extraction
B
57Fe/54Fe
56Fe/54Fe
56/54Fe
C
ln 57Fe/54Fe
ln 56Fe/54Fe
y = 1.5408x - 5.2622
R2 = 0.9814
y = 1.6009x - 5.4383
R2 = 0.9998

Figure 5

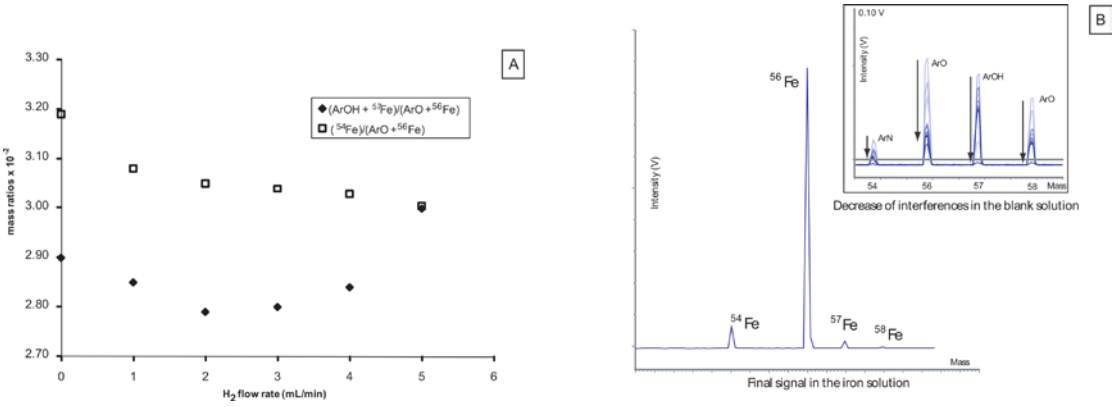


Figure 6

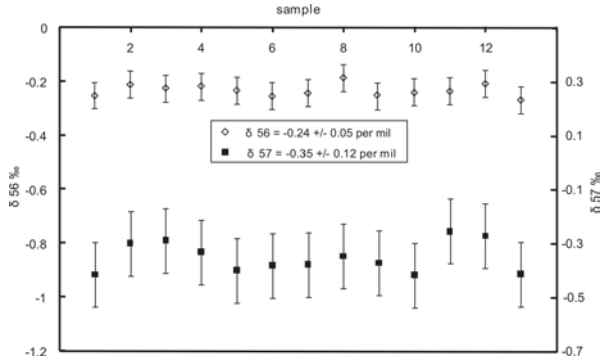


Figure 7

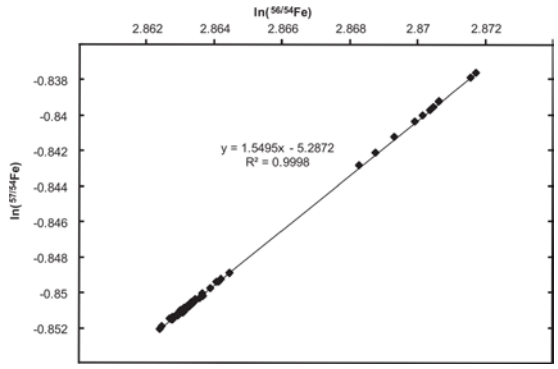


Figure 8